Full Paper

MULTISTAGE MINERAL ACID LEACHING DE-MINERALIZATION OF A MEDIUM CAKING COAL

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ABSTRACT

Coking coals are required to contain ash and sulphur contents that are less than 12% and 0.8% respectively. Preliminary test on Chikila coal gave high ash and sulfur contents of about 14.90% and 1.68%, the objective is to de-mineralize it using mineral acid._Sample of Nigerian Chikila coal obtained at a depth of about 4.5 m was air dried, crushed and pulverised. Fractions of -425+300 μm and -75 μm were leached with dilute hydrochloric acid using 2^4 factorial variables combination. Three multistage leaching were conducted. The filtrates and coal concentrate obtained were analysed using UV spectrophotometer and particle induced X-ray emission (PIXE) analyser, respectively. Sieve analysis showed a cumulative oversize of 63.3% at 600 μm mesh size, while the remaining 36.7 % were distributed on the lower sieves. The proximate analysis of the sample as-received gave moisture, volatile matter, ash, sulphur and fixed carbon percents 4.70, 42.12, 12.6, 1.68 and 40.58, respectively. The multistage leaching of -75 μm fraction using H_2O-HCl-H_2O sequence produced a coal concentrate with moisture, volatile matter, ash, sulphur and fixed carbon percents of 3.85, 34.52, 8.13, 1.02 and 53.50, respectively. This translates to a decrease in ash, sulphur and volatile contents of 35.48, 39.29 and 18.04 % and an increase in carbon content of 24.15 %. A successful upgrade of the leaching to pilot scale will make the coal available as a blend component for economical industrial cokemaking.

Keywords: *Coking, coal, leaching, multistage, concentrate*

1. INTRODUCTION

Coal is a solid but brittle, carbonaceous black sedimentary rock that burns. The primary constituents of coal are carbon, hydrogen, oxygen, nitrogen, lesser amounts of sulphur and other trace elements. Nigeria is endowed with notable coal deposits at Ogboyoga, Okaba, Orukpa, Ezimo, Enugu and Lafia-Obi with total reportable and non-reportable reserves of 411, 635, 299, 349, 209 and 33 million metric tons, respectively. Lafia-Obi is the only medium coking of the six coals but contains very high inherent ash and sulphur. Chikila coal is located in Guyuk Local Government area of Adamawa state and the reserve is not yet determined (Adeleke *et al.* 2007).

Prime grade coking coal is scarce worldwide. Upgrade of low grade coals by reducing their ash and sulphur contents is thus needed. There are physical, chemical and biological methods to upgrade coals with low ash, low sulphur and improved thermoplastic properties. The chemical leaching methods which include molten caustic leaching, agitation caustic leaching and mineral acid leaching have been successfully applied to coals (Ehinola and Adene, 2008; Obaje, 1997; Adeleke *et al.*, 2013). It has been established that mineral acids are effective leaching agents for ions of ash constituents found in coal. These ions include Ca^{2+}, Fe^{3+}, K^+, Mg^{2+}, Na^+, Al^{3+} and Mn^{2+} (Mehtap *et al.*, 2004).

The aim of this study is to evaluate the leaching effect of hydrochloric acid in a multistage leaching process on the high ash and high sulphur medium caking Chikila coal at normal atmospheric pressure.

2. MATERIALS AND METHODS

2.1. Materials

2.1.1. Sample Collection

Samples of Chikila coal obtained from Adamawa state was used for this research. Two tons of the coal was collected by the National Metallurgical Development Centre (NMDC) Jos, at a depth of about 4.5 m. About 4.6 kg working sample was prepared from the 8.6 kg sample collected from the NMDC bulk sample for this study.

2.1.2. Sample preparation

The 4.6 kg coal sample was crushed with Pascal Engineering 18862 primary crusher to obtain the experimental samples. A representative quantity of 500 g sample of the coal was taken by coning and quartering method for sieve analysis.

2.2. Methods

2.2.1. Experimental design

The single stage leaching was conducted using 2^4 factorial design. The experimental variables were; acid concentration (denoted by C), time of leaching (denoted by t), temperature of leaching (denoted by T) and coal particle size (denoted by S). The basis of the experimental design was that each of the four variables was used at 'high' levels (denoted by H) and 'low' level (denoted

by L). The experimental variables are used as subscript as either low (L) or high (H). The number of experiment in the design was 2^4 (i.e. 16). Using the above nomenclature, the various interacting combination among the variable used in the design were;
$L_T L_C L_t L_S$ (I) $H_T L_C L_t L_S$ (II) $L_T H_C L_t L_S$ (III)
$H_T H_C L_t L_S$ (IV) $L_T L_C H_t L_S$ (V) $H_T L_C H_t L_S$ (VI)
$L_T H_C H_t L_S$ (VII) $H_T H_C H_t L_S$ (VIII)
$L_T L_C L_t H_S$ (IX) $H_T L_C L_t H_S$ (X) $L_T H_C L_t H_S$ (XI)
$H_T H_C L_t H_S$ (XII) $L_T L_C H_t H_S$ (XIII) $H_T L_C H_t H_S$ (XIV) $L_T H_C H_t H_S$ (XV) $H_T H_C H_t H_S$ (XVI)

The values used for each variables at low and high level is presented in Table 1.

2.2.2. Particle size analysis

A representative quantity of 500 g sample of the coal was taken by coning and quartering method for sieve analysis. Standard nest of sieve was selected according to ASTM E-11 standard procedure for which six sieve sizes used were 600, 425, 300, 212, 150 and 75 µm, respectively. The sieves were arranged in a stack, with the coarsest sieve on top and the finest at the bottom. A tight-fitting pan was placed under the bottom sieve to receive the final undersize and a lid was placed on top of the coarsest sieve to prevent escape of the sample. The 500 g mass of sample was poured into the topmost sieve which had the largest screen openings. The column was placed in a mechanical shaker and vibrated for a period of 20 min. Thereafter, the fraction on each sieve was weighed and the weight of the sample remaining on each sieve was divided by the total weight to give a percentage retained on each sieve.

2.2.3. Proximate analysis

Proximate analysis was done to determine the percentage by weight of the fixed carbon, Volatiles matter, Ash, and Moisture Content in the coal using modified forms of methods described in ASTM D 3177-89 and Francis and Peters (1980).

2.2.4. Single stage leaching

Preliminary leaching was carried out on the coal samples using nitric, hydrochloric and sulphuric acids. About 1 g of +300 µm coal fraction was weighed into a 250 ml beaker containing 30 ml of 1 molar solution of nitric acid and carefully homogenized by stirring for about two minutes. The slurry was then placed in a Gallenkamp 7B 16590 oven maintained at 90 °C for 75 min. The leached slurry was filtered into a conical flask using a XingXing filter paper. The residue was collected, oven dried at about 80°C and then re-weighed. The difference in weight was noted for determining the fraction of coal that has been dissolved. This procedure was repeated for hydrochloric and sulphuric acids. The hydrochloric acid that gave the highest weight loss was then used for the 2^4 factorial single stage leaching. The single stage leaching was carried out following the design given in section 2.2.1 and the levels in Table 1. The first leaching involved $L_T L_C L_t L_S$. 1 g of the -75µm fraction was leached and filtered as described for nitric acid in the preliminary leaching stage but with 0.2 M HCl at 30°C for 20 min and in duplicates. The procedure was again repeated for other experimental designs.

2.2.5. Multistage leaching

The three-stage multistage leaching was carried out in three sequences that involved acid and water, that is: HCl-H_2O-H_2O, H_2O-HCl-H_2O and H_2O-H_2O–HCl. The first stage leaching and filtration in the HCl-H_2O-H_2O sequence was carried out as in the preliminary leaching stage using 1 M HCl for the 1 g -75 µm fraction sample at 90°C in 20 minutes contact time. The procedure was repeated on the residue concentrate obtained using H_2O. The latter water cleaning stage was again repeated as the third stage of the HCl-H_2O-H_2O sequence. The other two sequences was carried out following the description above but in order H_2O- HCl-H_2O and H_2O - H_2O – HCl. The sequence that gave the highest weight loss was noted. The filtrate and dried leached coal from this stage were taken for spectrophotometry and PIXE analysis.

2.2.6. UV Spectrophotometric analysis

The selected filtrates obtained were analyzed for sulphur using a UV-visible spectrophotometer (CECIL model no CE2502 2000 series). The calibration samples were prepared and the quartz cuvettes were rinsed with deionized water several times. 3 ml of sample were placed into cuvette using a pipette. The cuvette was wiped with very fine paper to remove any water droplets or dust and was then placed into the spectrophotometer and reading was taken (Woolins, 2010).

2.2.7. Particle induced X-ray emission analysis

The best multistage leached and as-received coal samples were subjected to particle induced X-ray emission analysis using 1.7MV Pelletron Tandem Accelerator model 5SDH, for sulphur. For each case, about 100 mg of the sample was ground into fine powder using a mortar and pestle. The powder was then compacted to 29-mm diameter pellets using a hydraulic press equipped with a case-hardened stainless steel die at 130 atm for 1 minute. Binding agent was added to the powder before pressing to make the pellet durable. The pellet was then mounted directly onto the target frame for irradiation. The X-ray spectrum was initiated by irradiating sample with a proton beam produced from pure Hydrogen by, in this case, a 1.7 MeV protons. The readings were shown on the display unit and printed.

Table 1: Levels of variables considered

Levels	Temperature (T, °C)	Concentration (C, M)	Time (t, Min)	Particle Size (S, µm)
Low	30	0.2	20	-75 µM
High	90	1	75	-425 +300

Table 2: Sieve analysis of Chikila coal

Sieve Number	Particle size range (µm)	Weight of sieves (g)	Mass of Sample retained (g)	Weight percent (%)	Cumulative undersize (%)
1	-75)	615.00	46.00	9.40	9.4
2	-150+75	334.00	5.50	1.10	10.5
3	-212+150	302.50	17.00	3.40	13.9
4	-300+212	309.50	23.00	4.60	18.5
5	-425+300	320.00	68.00	13.60	32.1
6	-600 + 425	366.00	23.00	4.60	36.7
7	+ 600	356.50	316.50	63.30	100.0

3. RESULTS AND DISCUSSION

3.1. Particle Size Distribution of Chikila Coal

Table 2 shows the particle size analysis of the coal as-received. The results obtained show that after the single stage crushing of the as-received coal lumps using standard coal pulverizer, the cumulative undersize at 600 µm was 36.70 %.

Retention of 63.30 % of the pulverized coal on the sieve with 600 µm size shows that Chikila coal could not be readily pulverized. This might be as a result of the high ash content of the coal. The bar chart gives a clearer picture of the sieve sizes and the retained percentages. Sieve size 75 µm with sieve number 2 retained the least sample of just 1.1 %. The last pan was able to receive just 9.40 % of the pulverized coal. The leaching process was carried out with samples retained on the 300 µm and 75 µm which are 13.60 % and 1.1 % respectively. The cumulative size distribution is presented in Figure 1. The curve displays the trend in which the retained sample rises with respect to sieve number, i.e. with decreasing sieve size.

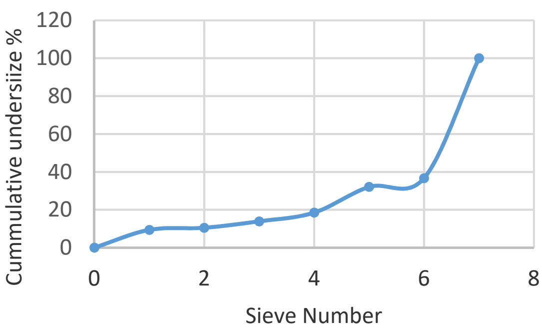

Fig. 1: Cumulative undersize distribution curve

The proximate analysis of the coal is shown in Figure 2. The moisture content in the as-received sample is 4.70%. This value of moisture content is high and would result in a decreased plant capacity and an increase in operating costs with consequent decrease in the calorific value of the coal (Jauro *et al.*, 2008). However, the best leached sample gave a lower moisture content of 3.85% indicating an improvement in the coal. But when compared to the moisture content required for good coking coal which is 1.5 %, the moisture content value is still high (Obaje, 1997). The required moisture content of coal to be used for metallurgical cokemaking is however expected to be between 1 % and 6 % (Leonard *et al.*, 1996). This shows that Chikila coal can still be used for metallurgical cokemaking. High and variable moisture contents affect both the coke rate and the balances within the blast furnace (Leonard *et al.*, 1996). The volatile matter present in the as-received sample is 42.12 %. This implies that there is high presence of methane, hydrocarbons, hydrogen, carbon monoxide and incombustible gases like carbon dioxide and nitrogen in the coal. The effect of this high value of volatile matter includes among others, proportionately increase in flame length and easier ignition of coal (Khan *et al.*, 2003).

However, the best leached sample gave a lower volatile matter content of 34.52 %. The reduction suggests that the volume originally occupied by volatile matter has been replaced by carbon thereby increasing the carbon content. The increase in carbon content is an indication of improvement in the coal quality. This is because it is a significant constituent of the coal required for coke making (Adeleke *et al.*, 2013). The Figure also shows the ash content of the as-received coal to be about 12.60%, which exceeds the allowable limit of 12% for coals to be carbonized to produce metallurgical grade coke (Leonard *et al.*, 1996). The coke ash is a nonproductive part of coke which increases slag volume and increase heat energy input for ironmaking. Industrial experience indicates that a 1 wt.% increase of ash in the coke reduces metal production by 2 or 3 wt.%. Ash content values higher than 10 wt.% can be satisfactory but only if the ash chemistry is acceptable (Leonard *et al.*, 1996). Other implications of high ash content in Chikila coal include reduction in handling and burning capacity, increase in handling costs, reduction in combustion and boiler efficiency, clinkering and excessive slagging (Poos, 1992). However, the best leached coal sample was found to have an ash content of 8.13 % making it suitable for appreciable inclusion in blends for cokemaking.

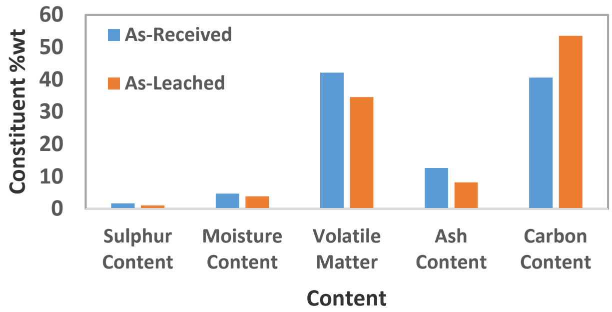

Fig. 2: Proximate analysis of Chikila Coal (as-received and as-leached multistage)

The as-received sample of Chikila coal has a fixed carbon of 40.58 %. The fixed carbon content of coal is used as an indication of the yield of coke in a coking system. The 40.58 % value of fixed carbon content in Chikila coal shows that the as-received sample of the coal will not yield a good coke because the value is very low (Nasirudeen and Jauro, 2011). However, the best leached sample has a higher fixed carbon content of 53.50%. This shows that the leaching has brought a significant increase to the fixed carbon content of the coal. The fixed carbon content of the leached Chikila coal is however lower than that of leached Lafia-Obi coal which is about 60% (Adeleke *et al.*, 2011).

3.2. Single Stage Leaching of Chikila Coal Using 2^4 Factorial

The results obtained from 2^4 Factorial single stage leaching with variables as described under Experimental Design is presented in Figure 3. It is observed that the highest weight loss of 11.8% was obtained when the leaching temperature is high, 90°C, the molar concentration of acid is high, 1 molar, the particle size of coal is low, ‹75 µm and the leaching time is low, 20 min. This shows that acid leaching has the greatest effect on Chikila coal when it is done at high acid concentration, high temperature and a very fine particle size of coal. The leaching was more potent at high concentration of acid because at high concentration of acid, more H^+ was available at the reaction surface with the oxide. Furthermore, the high temperature of 90°C promoted increased leaching because the kinetic of the leaching reaction at higher temperature. The best leaching yield was obtained with a particle size of -75 µm. This is a very fine particle size and the surface area available for the leaching reaction is optimum at this level. The explanation for this is that as the particle size decreases, the surface area of coal increases and the reaction rate definitely increases (Seferinoglu *et al.*, 2003).

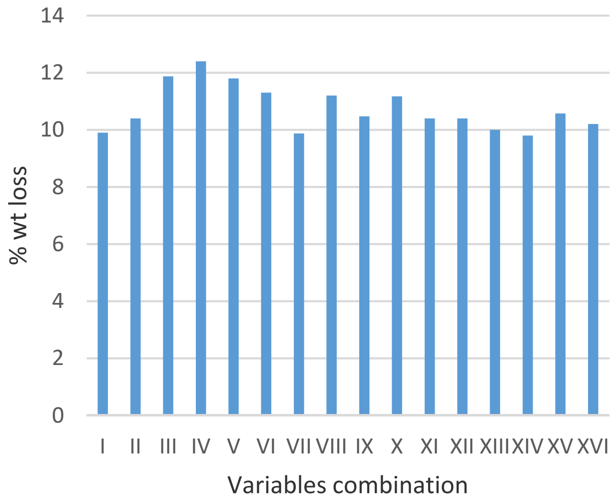

Fig. 3: Chikila coal single stage leaching using hydrochloric acid

3.3. Multistage Leaching

Results obtained from multistage leaching are presented in Figure 4, where TWL1, TWL2 and TWL3 are total weight loss for sequences 1, 2 and 3, respectively. The best yield for the multistage leaching was obtained with the combination of water and acid in the order; water-acid-water. The result shows that 13.87 % of the coal was leached out when the sequence was in the order H_2O-HCl-H_2O (W-A-W). This gives the greatest yield for the entire multistage leaching and single stage leaching. This observation agrees with the conclusion of Adeleke *et al.* (2011; 2013) that the H_2O-Na_2CO_3-H_2O leaching sequence gave higher ash and sulphur reductions in Lafia-Obi coal than the Na_2CO_3-H_2O-H_2O leaching sequence.

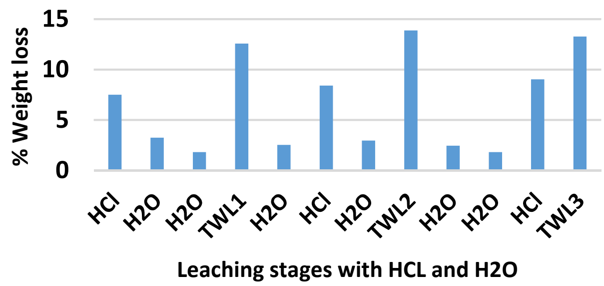

Fig. 4: Multistage leaching using HCl and H_2O in various sequences (TWL1, TWL2 and TWL3 are total weight loss for sequences 1, 2 And 3 respectively).

The reason for the higher leaching potency of the H_2O-HCl-H_2O sequence may be because in the route, the preliminary water washing might have prepared the coal matrix for the subsequent acid leaching, making it more efficient and the last water washing might have helped in dissolving some of the soluble product of the acid leaching. Dilute acid leaching has been shown to be an efficient method (Wu *et al.*, 2011). The multistage leaching thus gave a much higher weight loss than the 12.40% obtained for the single stage leaching.

3.4. Filtrate spectrophotometry analysis

The spectrophotometry analysis of the filtrates carried out for sulphur and presented in Table 3, indicates that the filtrate obtained from the multistage leaching process that involves H_2O – HCl – H_2O, contains highest amount of sulphur which is measured as 0.04 mg/g. This is considerably large in comparison to the ones obtained for other leachings presented in the table. This indicates that more sulphur was leached out of the coal through the multistage leaching of using the water-acid-water order of leaching.

Table 3: Filtrate spectrophotometry analysis

Sample	Sulphur conc. in milligram per gram of coal (mg/g)
Best HCl leached, Single Stage	0.027
H_2O – HCl – H_2O	0.040
H_2O – H_2O – HCl	0.037
HCl - H_2O – H_2O	0.033

3.5. Particle induced x-ray emission (PIXE) analysis

The results obtained from the PIXE analysis of the as-received coal sample and the water-acid-water leached coal sample (Table 4) when compared, indicate that the sulphur content of the coal has been reduced from 1.68 % to 1.02 %. This shows that using multistage leaching method, hydrochloric acid is an effective reagent that is capable of leaching sulphur out of Chikila coal. Furthermore, the concentration of selected metals whose oxides are the major ash constituents present in the coal samples has been reduced. These metals constituent in the coal were reduced because some of their oxides were able to dissolve in water and in the HCl used for the leaching.

Table 4: Concentration of relevant elements in the as-received Chikila coal sample

Elements	As-Received (mg/g)	(%)	H_2O-HCl-H_2O (mg/g)	(%)	% Change
Sulphur (S)	16.80	1.68	10.21	1.02	39.22
Sodium (Na)	3.71	0.37	-		-
Magnesium(Mg)	6.78	0.67	3.18	0.32	53.09
Silicon (Si)	77.08	7.70	76.69	7.67	0.51
Potassium (K)	2.89	0.29	1.99	0.20	31.14
Calcium (Ca)	8.62	0.86	2.64	0.26	69.37
Iron (Fe)	9.07	0.91	8.55	0.85	5.73
Titanium (Ti)	1.81	0.18	0.34	0.03	81.22

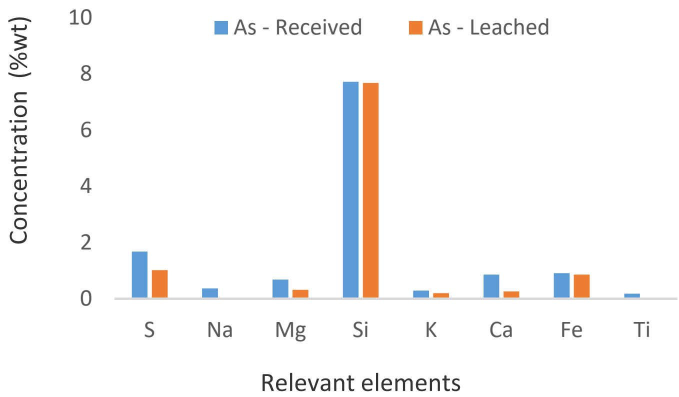

Fig. 5: Graphical view of the concentration of relevant elements in the as-received and as- leached coal sample.

4. CONCLUSION

The sulphur contents of the fractions of Chikila coal -75 µm were successfully reduced by multistage acid leaching that involved the use of HCl of 1 molar concentration and water. The reduction obtained for sulphur content from 1.68 % to 1.02 % is very significant and it indicates that Chikila coal can be used as a blend with low ash/sulphur prime grade coals for cost effective metallurgical cokemaking.

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